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Short range ordering in Fe–Ge and Fe–Ga single crystals

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We report on the nature of short range ordering (SRO) in slow cooled (100) and (111) $Fe_{81.6}Ga_{18.4}$ and $Fe_{81}Ge_9$ single crystals determined by x-ray θ-2θ scans. The SRO of the Ga atoms has at least some $D0_3$ character. In contrast Ge atoms only exhibit B2 chemical ordering symmetries in the short range order. It has been proposed that the $D0_3$ character in the SRO is important for the enhancement in magnetoelasticity in Fe-based alloys; however the presence of B2 character in Fe–Ge alloys suggest that the SRO is not of primary importance in increasing the magnetostriction. © *2009 American Institute of Physics*. [doi:10.1063/1.3254249]

The addition of nonmagnetic elements such as Al, Ga, and Ge into Fe significantly enhances the magnetostriction (MS) for Fe–Al,[1] Fe–Ga,[2] and Fe–Ge (Ref. 3) alloys. The MS increases monotonically with the solute concentration in the A2 single phase region and reaches a maximum near the solubility limit for these systems. Although extensive efforts have been made especially focused on Fe–Ga, the origin of the enhanced MS in these alloys is not well understood, and both extrinsic and intrinsic models have been proposed for the Fe–Ga. The extrinsic model[4] proposed a series transformations including (1) $D0_3$ precipitation from the parent bcc α-Fe, (2) transformation of $D0_3 \rightarrow D0_{22}$ (an intermediate tetragonal phase via a Bain distortion that shifts the atomic positions closer to their final positions in the $L1_2$ Fe_3Ga structure, and finally (3) precipitation of $L1_2$ Fe_3Ga. Using neutron scattering, Cao *et al.*[5] found an asymmetry and peak splitting in the short range ordering (SRO) peak of $D0_3$ in $Fe_{81}Ga_{19}$ alloy. Cao *et al.* argued that this has resulted from a tetragonal distortion of the $D0_3$ phase and is therefore consistent with the extrinsic model for the enhanced MS in Fe–Ga alloys. In contrast, Clark *et al.*[6] suggested that the enhanced MS in Fe-based alloys may be due to the presence of clusters or SRO of solute Ga atoms, which act as both elastic and magnetoelastic defects in the alloys. Cullen *et al.*[7] modeled the anisotropy of Fe–Ga alloys and suggested that $\langle 001 \rangle$ Ga pairs are responsible for the local magnetic anisotropy and the large MS. More recently, based on the experimental results of differential x-ray absorption spectroscopy in $Fe_{81}Ga_{19}$ alloy, Ruffoni *et al.*[8] proposed that the magnetostrictive strain in the vicinity of the $\langle 001 \rangle$ Ga–Ga pairs defects is responsible for the enhanced MS in Fe–Ga alloys, which is consistent with the first principle calculations prediction[9] that the B2-type (CsCl type) of local atomic arrangement is important in determining the degree of magnetoelastic coupling. We recently have used synchrotron x-ray diffuse scattering measurements to characterize the development of SRO as a function of Ga-composition and heat treatment.[10] Broad peaks at positions such as (100) and $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$, which are forbidden by the BCC structure while allowed by the $D0_3$ structure, were observed to grow rapidly with increasing Ga. In both quenched and slow cooled samples, MS decreased rapidly when SRO clusters grew beyond a characteristic size.

In order to understand how SRO relates to the MS and the mechanism of the enhanced MS in Fe-based alloys, it is necessary to investigate alloys in other systems. Fe–Ge is a particularly good candidate because, on one hand, it is similar to Fe–Ga in which there is an A2 phase region with appreciable solubility. On the other hand, based on published phase diagrams, the neighboring phase to the α-Fe is an ordered B2 (Ref. 11) instead of $D0_3$ or $L1_2$ present in Fe–Ga.[11,12] Furthermore, unlike the complexity and metastability of the phases present in Fe–Ga alloys with Ga$>\sim$18 at. %, the phase relations in Fe–Ge system is relative simple and reproducible, resulting in magnetostrictive response that is not thermally dependent.

In this letter we report on the differences in the SRO between $Fe_{81.6}Ga_{18.4}$ and $Fe_{91}Ge_9$ single crystals measured by x-ray θ-2θ scans on slow cooled (100) and (111) single crystalline specimens. The use of single crystals in characterizing the SRO in Fe–Ga and Fe–Ge alloys is necessary because of the similar scattering factors of Fe, Ga, and Ge that lead to an extremely weak intensity of SRO peaks. However, using the θ-2θ x-ray scans on oriented single crystals in structure determination has certain limitations. For example, for a given orientation, only a subset of the reflections will be observed, based on the orientation of the crystal and allowed reflections for a given crystal structure. For instance, a (100) oriented crystal will diffract from planes of the family (h00), and for a (111) single crystal, only reflections associated with the (hhh) planes will be diffracted. Table I shows the allowed reflections for the possible phases in these two systems in the composition range of interest. By analyzing different orientations, the nature (symmetry elements) of the SRO can be determined by either the presence or absence of diffuse scattering peaks usually located at the superlattice peak positions that are unique to each structural form and orientation. Another complication to the use of single crystals in the Bragg–Brentano geometry is that mosaic structure will also lead to the peak shifts, peak splitting, and/or peak asymmetry.[13] Fe–Ga single and polycrystals can exhibit a high degree of mosaicity.[14,15]

Slabs of (100) and (111) oriented single crystals of $Fe_{81.6}Ga_{18.4}$ and $Fe_{91}Ge_9$ were sectioned from the ingots. The sample size was $10\times10\times2$ mm^3. Oriented samples were prepared using standard metallographic procedures with the final polishing step using diamond paste, followed by a Nital etch. The last step was found to be crucial in the removal of

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TABLE I. Occurrence of various x-ray diffraction reflections in oriented single crystals for the structural variations present in the Fe–Ga alloy system. The unit cell doubling of $D0_3$ phase results in the appearance of superlattice peaks having half integer indices.

Crystal structure				2θ		
A2	B2	$D0_3$	$L1_2$	(°)	(100) crystal	(111) crystal
			100	24.26	√	
		$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$		26.60		√
	100	100		30.81	√	
			110	34.58		
			111	42.69		√
110	110	110		44.14		
			200	49.71	√	
	111	111		54.79		√
200	200	200		64.19	√	

surface damage layers, which can lead to the appearance of anomalous reflections.[16] Orientation was done by back-reflection Laue diffraction to within ±0.25° of the desired orientation. X-ray diffraction scans were conducted using a Panalytical X'Pert diffractometer with Cu $K\alpha$ radiation at 45 kV and 40 mA.

Figure 1 shows (100) scan for $Fe_{81.6}Ga_{18.4}$ and $Fe_{91}Ge_9$ alloys. It can be seen from Fig. 1 that (i) a strong peak exists at around 64° corresponding to the fundamental (200) reflection of the A2 phase; (ii) the intensity of the diffuse scattering peaks at around 28°–34° is extremely weak compared with the (200) fundamental peak; and (iii) the diffuse SRO peak for Fe–Ga is symmetric, but that for Fe–Ge is asymmetric as shown in the insets. The SRO peaks observed in the present study are considerably narrower with much lower relative intensity than those reported by Guruswamy *et al.*[17] Those broad diffuse peaks in the 2θ range of 20°–42° may be due to the surface damage because the distorted/disturbed layers formed during the surface preparation could lead to observation of false structure (artifact). Similar broad peaks were observed in our laboratory for highly polished single crystalline samples without acid etching to remove surface damage. The effect of removing the surface damage layers on x-ray results will be discussed more in detail in the (111) crystals.

Using the position of the (200) reflection, the lattice parameter was determined as a=2.9035(5) and 2.8817(0) Å for $Fe_{81.6}Ga_{18.4}$ and $Fe_{91}Ge_9$ alloys, and accordingly, the angle

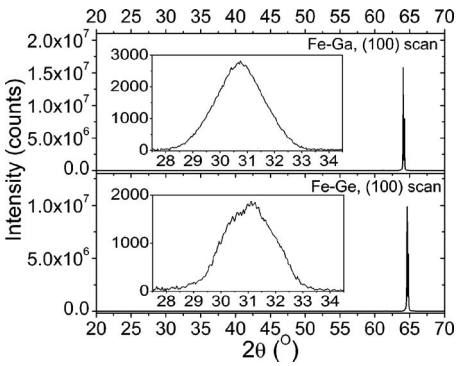

FIG. 1. X-ray diffraction patterns of $Fe_{81.6}Ga_{18.4}$ and $Fe_{91}Ge_9$ alloys scanned on (100) crystals. The insets show diffuse scattering peaks at (100) superlattice reflection.

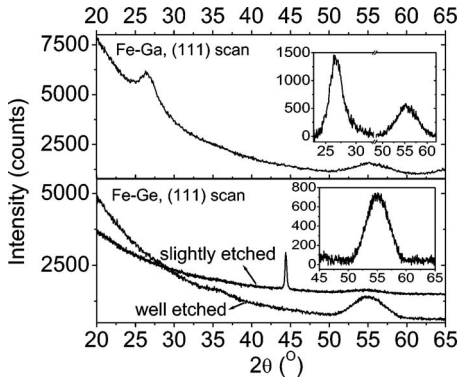

FIG. 2. X-ray diffraction patterns of $Fe_{81.6}Ga_{18.4}$ and $Fe_{91}Ge_9$ alloys scanned on (111) crystals. The insets are the background removed patterns. $D0_3$ and B2 SRO peaks were observed for $Fe_{81.6}Ga_{18.4}$ and $Fe_{91}Ge_9$, respectively.

for (100) superlattice reflection was determined as 30.768° and 31.007°, respectively. The SRO peaks centered at 30.703° and 31.019° are shifted −0.065° and 0.012° with respect to the superlattice peak for Fe–Ga and Fe–Ge, respectively. This negligible shift in the SRO peaks with respect to the superlattice peaks indicates that no significant stress/distortion is present in the lattice, which is in consistent with our previous study that SRO peak coincides with the superlattice peak as Ga content approaches the solubility limit of the A2 phase.[10] The correlation length determined from the full width at half maximum of (100) SRO peak is ~4.3 and ~3.6 nm for Fe–Ga and Fe–Ge, respectively. These values compare well to previously reported values[10] of correlation lengths using synchrotron x-ray scattering for slow cooled $Fe_{81.7}Ga_{18.3}$ alloy (~3.8 nm) but about three to four times larger than that reported by Cao *et al.*[5] using neutron scattering.

The appearance of diffuse but relatively narrow scattering peaks at the forbidden reflection indicates short range chemical ordering of Ga and Ge atoms in the bcc iron lattice. However, since the (100) superlattice reflection is allowed for both $D0_3$ and B2 in (100) crystals, it is not possible to discern the symmetry (average local atomic arrangement) from these diffuse scattering peaks. Therefore, scans on (111) crystals were conducted as shown in Fig. 2. It can be seen that (i) a sharp peak is observed at around 44° in the slightly etched Fe–Ge crystal only but is not present in well etched Fe–Ge and Fe–Ga crystals; (ii) two diffuse peaks, one at ~26.5° $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and the other one at ~55° (111), were observed for Fe–Ga alloy but only (111) reflection (~55°) was observed for the Fe–Ge alloy; and (iii) both SRO peaks in Fe–Ga are asymmetric, but the SRO peak in Fe-Ge is symmetric. The sharp peak at ~44° [corresponding to the (110) fundamental peak, which is not allowed for the (111) crystal in this geometry] has been observed previously.[16,17] Similarly, full Debye rings have been observed in diffuse scattering images of single crystalline Fe–Ga alloys using synchrotron x-rays in a transmission mode. The Debye rings on single crystalline alloys, the dependence of peak intensity on the degree of etching, and the absence of this peak in the well etched Fe–Ge and Fe–Ga alloys all suggest that this anomalous scattering is due to the surface damage during sample preparation. This type of scattering could arise from either plastic deformation or an undetermined strain induced transformation.[4,16]

Since a B2 superlattice reflection is forbidden at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ reflection (~26.5°), as shown in Table I, the absence of SRO peak at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ reflection in the scan on the (111) Fe–Ge crystal indicates that the SRO of Ge atoms in Fe–Ge alloys has symmetry elements consistent with B2 chemical ordering (strong nearest neighbor interactions). Accordingly, the existence of a diffuse scattering peak at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ reflection (~26.5°) in Fe–Ga alloys indicates that both first and second nearest neighbor interactions are important and the SRO of Ga atoms in Fe–Ga has symmetry elements consistent, at least in part, with $D0_3$ chemical ordering.[10]

Several other aspects of the superlattice reflections show interesting differences between Fe–Ge and Fe–Ga crystals. First, the (100) SRO peak in Fe–Ge is asymmetric, but the (100) SRO peak in Fe–Ga is not, whereas the reverse is observed for the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and (111) SRO peaks in Fe–Ga versus Fe–Ge. The peak asymmetry in SRO peak in single crystals could be related to mosaic structure, stress, or size effect. The negligible peak shift with respect to the superlattice reflection indicates that there is no significant stress or size effect at these compositions. The peak asymmetry has also be attributed to the tetragonal distortion as suggested by Cao *et al.*[5] However, the peak asymmetry observed in the present study for the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and (111) SRO peaks in Fe–Ga can rule out this possibility because a tetragonal distortion will not lead to peak asymmetry in (*hhh*) reflections for a cubic crystal. Therefore, the asymmetry observed in the present study is not consistent with tetragonal distortion and is most likely resulted from the as-grown mosaic structure present in the single crystals.[13–15]

In summary, we have investigated the SRO in $Fe_{81.6}Ga_{18.4}$ and $Fe_{91}Ge_9$ single crystals. The SRO of Ga atoms in Fe–Ga has $D0_3$ and B2 chemical ordering tendencies, while that of Ge atoms in Fe–Ge alloys has only B2 chemical ordering tendency. The B2 SRO found in Fe–Ge is not necessarily consistent with the mechanism of enhanced MS proposed by the extrinsic model,[4] suggesting that an alternative mechanism is responsible for the increases in MS in Fe–Ge alloys.

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